



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB90/01450 <b>(22) International Filing Date:</b> 20 September 1990 (20.09.90) <b>(30) Priority data:</b> 8922504.9                      5 October 1989 (05.10.89)                      GB <b>(71) Applicant (for all designated States except US):</b> INTEROX CHEMICALS LIMITED [GB/GB]; 3 Bedford Square, London WC1B 3RA (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> McDONOGH, Colin, Frederick [GB/GB]; 36 Willow Lane, Appleton Park, Warrington, Cheshire WA4 5DZ (GB). <b>(74) Agent:</b> PEARCE, Timothy; Group Patent Department, La- porte Industries Limited, Moorfield Road, Widnes, Cheshire WA8 0JU (GB).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), KR, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HYDROGEN PEROXIDE SOLUTIONS  <b>(57) Abstract</b>  It would be desirable to replace nitric acid based solutions for surface treating steels and like materials with a sulphuric acid based solution containing hydrogen peroxide, but such replacement solutions lose hydrogen peroxide rapidly through mainly iron-induced decomposition. A surface treatment solution that is based on sulphuric acid and hydrogen peroxide, but has improved stability, contains an effective amount in combination of hydrofluoric acid, a hydroxybenzoic acid and an N-alkoxyphenyl-acetamide. Preferably, the hydroxybenzoic acid is para-hydroxybenzoic acid and the N-alkoxyphenyl-acetamide is N-(4-ethoxyphenyl)-acetamide. It is preferable to employ a saturated solution of each of the two latter components, and this can be achieved practically and simply by adding the solid components in the shape of a block or blocks which maintain the saturated solution over an extended period of time.		

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### Hydrogen Peroxide Solutions

The present invention relates to hydrogen peroxide solutions and more particularly to a process for its stabilisation. In a further aspect, the present invention  
5 also relates to a stabiliser system for aqueous hydrogen peroxide solutions that are intended for use in metal surface treatments.

One of the many uses for hydrogen peroxide solutions, and especially aqueous acidic hydrogen peroxide solutions,  
10 comprises the treatment of metal surfaces so as to alter their appearance and to impart chemically to the surface a desired sheen or polish. This is often referred to simply as pickling or polishing. Conventionally, solutions for that use contain one or more strong acids, which is normally  
15 a mineral acid, as well as the hydrogen peroxide. In the course of the metal surface treatment, there is a tendency for the solution to dissolve metal or impurities from the metal surface and to strip away particulate particles that had adhered to the metal surface before the treatment  
20 commenced. The metals that are pickled or polished usually comprise or contain at least a proportion of transition metals, such as iron or copper, which catalyse the wasteful decomposition of hydrogen peroxide in aqueous solution into oxygen and water.

25 In view of its decomposition in situ, hydrogen peroxide often represents the major consumable cost in a pickling or polishing process. In consequence, the industry continues to seek ever more effective ways of reducing the rate and/or extent of the decomposition. In many instances, it has  
30 been sought by introducing into solution one or more

substances that are often called stabilisers, which interact with the metal ions and/or metal surface and/or the hydrogen peroxide itself in such a way as to reduce the rate or extent or modify the manner of the interactions between the metal ions and hydrogen peroxide causing decomposition.

There have been many different chemical types of stabilisers proposed or employed. The literature directed to peroxide stabilisation during metal surface treatment processes includes many organic compounds as stabilisers such as a range of organic acids or unsaturated aliphatic acids in USP 3 537 895 by L E Lancy, aromatic alcohols or unsaturated aliphatic alcohols in USP 3 869 401 by R E Ernst, saturated alcohols in USP 3 556 883 by A Naito et al, amines, amides and imines in USP 3 756 957 by S Shiga, aryl sulphonic or sulphamic acids or related compounds in USP 3 801 512 by J C Solenberger et al and solid poorly soluble stabilisers like hydroxybenzoic acid in USP 4 770 808 by C F McDonogh et al. Many other stabilisers have been suggested for peroxide solutions including substances that chelate the metal ions or precipitate them out of solution, for example in USP 4 059 678 to D C Winkley. The literature also includes references to inorganic substances, such as phosphoric acid in USP 3 373 113 to Achenback. Accordingly there is a wide pool of stabilisers from which the user can select.

Despite the foregoing, the present inventors found that there remains a significant problem of stabilising hydrogen peroxide during the metal surface treatment of steel with aqueous sulphuric acid solutions of hydrogen peroxide. This is because the greater part of the literature was directed to the treatment of copper surfaces and the authors extrapolated to the treatment of other metals without adequate experimental support. To some extent, this is demonstrated in USP 3 407 141 to R S Banush et al, which seeks to etch copper with acidic hydrogen peroxide solutions of long storage life that contain certain urea and aromatic acid compounds. The specification suggests that the

treatment can be applied to certain other metals but also that the solutions are less effective on certain other metals such as ...stainless steel... Since the patent disclosed results solely with copper, comments regarding other metals may be regarded simply as speculation.

In the course of the present research to identify, if possible, a suitable stabiliser system for acidic hydrogen peroxide solutions which are severely contaminated with dissolved iron, resulting for example from the surface treatment of steels, a large number of comparative stability trials were conducted. Each trial employed a stock solution containing 180 g/l sulphuric acid and 50 g/l hydrogen peroxide and 1% w/w "stabiliser" which was contaminated with 25 g/l dissolved iron from ferric sulphate, and stored at 30°C or 50°C. Many of the substances tested fell within the classes of stabilisers identified in the above-mentioned patent specifications.

The trials indicated that many substances which had been described in the past as stabilisers for hydrogen peroxide in solutions containing only small amounts of catalytic ions, were unable to prevent rapid decomposition if substantial iron contamination was present, including chelating stabilisers like ethylenediaminetetraacetic acid, dipicolinic acid, nitrilotriacetic acid and ethylenediamine-1,1-dihydroxy-1,1-diphosphonic acid. Moreover, it was found that some substances that acted quite well as stabilisers when employed separately, acted no better or even less well when employed in combination under the conditions of the trial. Other combinations of substances demonstrated strictly additive stabiliser properties. Accordingly, the trials demonstrated that a disclosure in a published patent specification that a substance had stabiliser properties towards hydrogen peroxide under much less extreme conditions or in the presence of copper as the main catalytic contaminant was no guarantee that it was capable of performing adequately in the presence of a substantial concentration of dissolved iron. The trials also

demonstrated that there was no guarantee that substances that had been suggested individually as stabilisers, possibly guarding against other sources of decomposition, would combine together even additively when employed in combination.

It is an object of the present invention to locate a combination of substances which could stabilise hydrogen peroxide effectively in aqueous sulphuric acid solutions that are employed in the surface treatment of steel and therefore become contaminated with significant concentrations of iron.

According to a first aspect of the present invention there is provided a process for stabilising an aqueous solution of hydrogen peroxide containing at least 1% w/w sulphuric acid which are suitable for treating the surface of steel and like alloys characterised in that there is introduced into the solution an effective amount, in combination of hydrofluoric acid, hydroxybenzoic acid and an N-alkoxyphenyl-acetamide.

According to a related aspect, there is provided a stabilised aqueous solution of hydrogen peroxide containing at least 1% w/w sulphuric acid and an effective amount in combination of hydrofluoric acid, hydroxybenzoic acid and an N-alkoxyphenyl-acetamide.

According to a further and related aspect of the present invention there is provided a process for the surface treatment of steel or a like alloy in which the latter is contacted with an aqueous solution of hydrogen peroxide containing at least 1% w/w sulphuric acid characterised in that it contains an effective amount in combination of hydrofluoric acid, hydroxybenzoic acid and an N-(alkoxyphenyl)-acetamide.

In the context of the present invention, the stabiliser combination comprises hydrofluoric acid, an aromatic acid and an aromatic amide. The hydroxybenzoic acid is particularly preferably p-hydroxybenzoic acid and the N-(alkoxyphenyl)-acetamide, advantageously, contains a low molecular weight

alkanoxy substituent and especially the compound is N-(4-ethoxy-phenyl)-acetamide.

Without being bound to any particular theory, the inventors believe that the components of the stabiliser system form a range of fluoride-containing complexes with iron and other ions that pass into solution during surface treatment of steels. The properties of these complexes, and in particular their interaction with hydrogen peroxide are believed to dictate the stability and hence extent of decomposition losses of hydrogen peroxide during the surface treatments. Furthermore, the presence of hydrofluoric acid is believed to provide the potential for the iron complexes to be significantly different from corresponding complexes in the absence of hydrofluoric acid and that this may explain to at least some extent why it is so difficult to apply teaching given for other solutions in the prior art and teaching on individual components in respect of the combination of the present invention.

The solution preferably contains from 0.5 to 10% w/w hydrofluoric acid and advantageously from 1 to 6%.

The concentrations of the aromatic acid and the aromatic amide in solution are each preferably at least 0.5 g/l and most preferably at or near saturation. Since they tend to be relatively poorly soluble, saturation can be attained by introduction of about 1g/l up to a few g/l of each.

In one preferred method of employing the invention stabiliser combination, advantage is taken of the physical properties of the two aromatic components, namely the acid and amide. In the preferred method, these two components are selected on the bases of their melting point and solubility. Specifically, it is preferable to select an acid and an amide which does not melt until a temperature significantly in excess of about 70°C is attained and which are scarcely soluble in an aqueous acidic medium. Such compounds will naturally be solids in the normal range of operating temperatures for hydrogen peroxide-based steel surface treatments and can dissolve to form a dilute, but

saturated solution. It is especially desirable to incorporate an excess amount of the aromatic acid and amide beyond that needed for a saturated solution so as to provide within the treatment bath a solid phase, a reservoir which can replenish the saturated solution as the compound is removed by the normal operation of the metal surface treatments, including in situ oxidation and by adhesion to the surface of the workpiece on separation from the bath. It will be recognised that both the above-named aromatic acid and aromatic amide demonstrate both such preferred characteristics, thereby rendering them especially attractive for this preferred method.

Whilst it is conceivable to incorporate such solids in the metal surface treatment solution in powder or granular form, there is a distinct tendency for that form of solids to be lost by carry out from a surface treatment bath. Powders are not easy to observe, so that it can be difficult to know how much of the solids are still present and in the extreme case whether any is present at all. Accordingly, in a more preferred mode of operation, the two solid poorly soluble components of the stabiliser system are each employed in the form of a block containing either an individual component or a mixture of them. The block is much easier to detect than is the corresponding amount of powder or flakes, either visually or by a non-manual system. Accordingly, regulation of the solid stabilisers in the treatment bath can be accomplished without recourse to elaborate and expensive monitoring equipment, whilst still minimising the possibility that the bath would be left without the organic components of the stabiliser system.

The term "block" is used in its normal dictionary meaning, as in USP 4 770 808, and covers a wide range of sizes. It typically has a weight of at least 30g and up to a few kg weight, eg 10kg. For many practical purposes, it weighs initially from 200g to 5kg, but will slowly be consumed during operation of the bath.

The block is normally obtained by compression or binding



of flakes, granules or powders into a tablet shape or in some other mould shape such as cube, cuboid polyhedron or cylinder, or by resolidification of a melt in such a mould or by extrusion of a rod or bar. Such techniques are well known in the field of tablet or block formation and accordingly need not be described in further detail herein.

The hydrogen peroxide solution is often described as a dilute solution. It normally contains at least 1% w/w hydrogen peroxide and it is unusual for it to contain more than 10% w/w. For the treatment of steels, it is often convenient to select within the range of from 3 to 8% w/w hydrogen peroxide. During normal operation, peroxide is consumed, so that without corrective means, its concentration would gradually diminish. At the discretion of the user, he can seek to maintain a steady state by introducing peroxide gradually at a rate that matches its consumption, including decomposition, or he can permit the concentration to fluctuate by augmenting the peroxide concentration periodically. The metal treatment solution is most conveniently obtained by the dilution of a concentrated commercial hydrogen peroxide solution, typically containing from 35 to 70% w/w hydrogen peroxide and trace amounts, ie below about 0.1% of known storage stabilisers such as pyrophosphate and/or stannate and/or polyphosphonic acid compounds.

The sulphuric acid concentration in the solution is normally not higher than 20% v/v and in many instances is conveniently selected in the region of 5 to 15% v/v.

The solution can also include minor amounts of the customary additives in metal treatment solutions, such as up to about 2% w/w wetting agents.

The processes using the stabilised hydrogen peroxide solutions of the present invention are normally carried out at a bath temperature of above ambient, and in many instances in the range of from 40°C to 70°C. Higher temperatures of up to about 80°C are less often encountered, but become more attractive as a result of the stabilisation

of the hydrogen peroxide component in the bath.

The residence period for the work-piece in the treatment bath is at the discretion of the user and naturally depends on the finish that it is desired to achieve. Residence  
5 periods are often selected in the range of from 30 seconds to 30 minutes, and normally from 1 to 5 minutes.

The stabilised acidic hydrogen peroxide solutions are primarily intended for the pickling or polishing of steels, including mild steel and is of especial value for treating  
10 stainless steels. Steels suitable for treatment by the invention process and compositions can contain minor proportions of such metals as chromium, nickle, and manganese; ie the metals that are incorporated in corrosion-resistant or stainless steels.

15 It will be recognised that the process and compositions according to the present invention can be employed instead of nitric acid-containing metal treatment compositions, thereby avoiding the problems of NO<sub>x</sub> emissions that accompany the use of nitric acid.

20 Having described the invention in general terms, specific embodiments thereof will now be described in more detail by way of example only.

#### Example 1 and Comparisons CA to CC

In this Example and these comparisons, the effectiveness of  
25 the invention combination of stabiliser components is compared under the same conditions of high dissolved iron with stabiliser-free pickling solution and solution containing components of the combination. In each trial, a solution was prepared which contained 5% w/w hydrogen  
30 peroxide, 10% v/v sulphuric acid, and 1.8% w/w ferric iron, added as ferric sulphate and the stabiliser(s) listed in Table 1 below were then mixed into the solution. The solid stabilisers are referred to by their abbreviations; PHBA for p-hydroxybenzoic acid and NEPA for N-(4-ethoxy-phenyl)-  
35 acetamide. Although the hydrofluoric acid was entirely miscible with the solution, the solid stabilisers did not dissolve completely, forming a saturated solution of the two

compounds and leaving a residue of solid material.

The solutions were then kept at 30°C and the residual hydrogen peroxide content was measured at intervals by the standard potassium permanganate method. Table 1 below

5 indicates the half life of the hydrogen peroxide in the solution, by which herein we mean the time taken for the measured hydrogen peroxide to fall to half its initial concentration.

Table 1

10 Example Comp No	Stabiliser System g/l			Half-life of H <sub>2</sub> O <sub>2</sub> hours
	HF	PHBA	NEPA	
CA	-	-	-	2
CB	40	-	-	3
15 CC	-	5	5	8
Ex1	40	5	5	>300

From Table 1, it can be seen that the effect of employing either the HF alone or the solids alone resulted in some improvement in peroxide stability, but their use in  
20 combination resulted in a very substantial improvement, well in excess of a simple additive effect. This shows that the combination is particularly effective in the presence of substantial concentrations of iron in solution, as would arise from the surface treatment of steel and like alloys.

#### 25 Examples 2 to 5

In these Examples, Example 1 was repeated, but using respectively a total weight of PHBA and NEPA (wt ratio 1:1) of 5 g/l, 10 g/l, 15 g/l and 20 g/l, HF at 40 g/l, 12.5% by volume sulphuric acid (98% w/w), about 50 g/l hydrogen  
30 peroxide and 29 g/l iron introduced as ferric sulphate. Within the limits of experimental variation, all four amounts of stabilisers resulted in a similar and high proportion of hydrogen peroxide being retained, viz about 82% after 43 hours. This is consistent with PHBA and NEPA  
35 forming saturated solutions at all four stabiliser amounts tested. To the extent that any trend was apparent, the most efficacious amount was the smallest.

Examples 6 to 11.

In these Examples, a solution was prepared which contained 5% w/w hydrogen peroxide, 10% v/v sulphuric acid, 1.8% w/w ferric iron, added as ferric sulphate and 10 g/l of a mixture of PHBA and NEPA in the proportions by weight listed in Table 2. The solutions were stored at 50°C in order to obtain the comparative results quickly, and residual hydrogen peroxide contents measured at intervals, as for Example 1. Table 2 indicates the percentage remaining after 24 hours.

Table 2

Ex No	Ratio of NEPA:PHBA	% peroxide remaining
6	2.3:1	46
7	1:1	42
15 8	1:4	53
9	1:9	43
10 10	1:24	45
11	9:1	32

From Table 2, it can be seen that the combination of HF plus NEPA plus PHBA remained a very effective stabiliser over a wide range of ratios of NEPA to PHBA, and especially in Examples 6 to 10 in which the amount of each of the two solid components was sufficient to ensure a saturated solution of each.

Example 12

In this Example, Example 7 was repeated but employing a solution containing additionally chromium at a concentration of 5 g/l, introduced as chromic sulphate. Within the limits of experimental variations, the proportion of hydrogen peroxide remaining in solution after 24 hours storage at 50°C was the same as in the absence of the chromium. This demonstrates that the stabiliser system is applicable for use in the surface treatment of stainless steels. In other comparative tests carried out with varying additions of chromium to an iron contaminated sulphuric acid/peroxide solution containing the invention stabiliser system, there was a tendency for the stabilisation to become

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somewhat impaired as the concentration of chromium was increased from 5 to 20 g/l.

## Claims:-

- 1 A process for stabilising an aqueous solution of hydrogen peroxide containing at least 1% v/v sulphuric acid which is suitable for treating the surface of steel and like alloys characterised in that there is introduced into the solution an effective amount, in combination of hydrofluoric acid, hydroxybenzoic acid and an N-alkoxyphenyl-acetamide.
- 2 A stabilised aqueous solution of hydrogen peroxide containing at least 1% v/v sulphuric acid and an effective amount in combination of hydrofluoric acid, hydroxybenzoic acid and an N-alkoxyphenyl-acetamide.
- 3 A process for the surface treatment of steel or a like alloy in which the latter is contacted with an aqueous solution of hydrogen peroxide containing at least 1% v/v sulphuric acid characterised in that it contains an effective amount in combination of hydrofluoric acid, hydroxybenzoic acid and an N-(alkoxyphenyl)-acetamide.
- 4 A composition or process according to any preceding claim characterised in that the sulphuric acid solution contains from 0.5 to 10% w/w hydrofluoric acid.
- 5 A composition or process according to claim 4 characterised in that from 1 to 6% w/w hydrofluoric acid is present.
6. A composition or process according to any preceding claim characterised in that the hydroxybenzoic acid and the N-alkoxyphenyl-acetamide are each present in a saturated solution.
7. A composition or process according to any preceding claim characterised in that the hydroxybenzoic acid is

para-hydroxybenzoic acid.

8. A composition or process according to any preceding claim characterised in that the N-alkoxyphenyl-acetamide is N-(4-ethoxy-phenyl)-acetamide.
9. A composition or process according to any preceding claim characterised in that the hydroxybenzoic acid and the N-alkoxyphenyl-acetamide are each contacted with the sulphuric acid solution in a weight ratio of from 25:1 to 1:5.
10. A process or composition according to any preceding claim characterised in the hydroxybenzoic acid and the N-alkoxyphenyl-acetamide are contacted with the sulphuric acid solution in the form of a block or blocks.
11. A process for the stabilisation of hydrogen peroxide in sulphuric acid solutions containing significant concentrations of iron or stabilised solutions of hydrogen peroxide in aqueous sulphuric acid or a metal surface treatment process employing a stabilised sulphuric acid solution of hydrogen peroxide substantially as described herein with respect to any novel feature or novel combination of features.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 90/01450

<b>I. CLASSIFICATION F SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 23 G 1/08, C 23 F 1/28, C 23 F 3/06																							
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: top; border: 1px solid black;">IPC<sup>5</sup></td> <td style="border: 1px solid black;">C 23 G, C 23 F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>5</sup>	C 23 G, C 23 F																	
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>10</sup></th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">FR, A, 2216222 (FMC CORP.) 30 August 1974 see claim 1; page 16, example 5 &amp; US, A, 4059678 cited in the application --</td> <td style="vertical-align: top; border: 1px solid black;">1</td> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">US, A, 3537926 (G. FISCHER) 3 November 1970 --</td> <td></td> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">FR, A, 2551465 (FORGES DE GUEUGNON S.A.) 8 March 1985 --</td> <td></td> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">EP, A, 0219945 (INTEROX CHEMICALS) 29 April 1987 &amp; US, A, 4770808 cited in the application --</td> <td></td> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">US, A, 3756957 (S. SHIGA) 4 September 1973 cited in the application --</td> <td></td> </tr> <tr> <td style="vertical-align: top; border: 1px solid black;">A</td> <td style="border: 1px solid black;">US, A, 2086123 (H.I. EISENMAN) 6 July 1937 -----</td> <td></td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	FR, A, 2216222 (FMC CORP.) 30 August 1974 see claim 1; page 16, example 5 & US, A, 4059678 cited in the application --	1	A	US, A, 3537926 (G. FISCHER) 3 November 1970 --		A	FR, A, 2551465 (FORGES DE GUEUGNON S.A.) 8 March 1985 --		A	EP, A, 0219945 (INTEROX CHEMICALS) 29 April 1987 & US, A, 4770808 cited in the application --		A	US, A, 3756957 (S. SHIGA) 4 September 1973 cited in the application --		A	US, A, 2086123 (H.I. EISENMAN) 6 July 1937 -----	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																							
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="height: 40px; vertical-align: top; border: 1px solid black;">18th December 1990</td> <td style="border: 1px solid black; text-align: center;">21 JAN 1991</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorised Officer</td> </tr> <tr> <td style="text-align: center; border: 1px solid black;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; border: 1px solid black;">MISS T. TAZELAAR</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	18th December 1990	21 JAN 1991	International Searching Authority	Signature of Authorised Officer	EUROPEAN PATENT OFFICE	MISS T. TAZELAAR													
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-B- 473299	17-06-76
		AU-A- 6479974	24-07-75
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		GB-A- 1451415	06-10-76
		JP-A, B, C 49106995	11-10-74
		NL-A- 7401261	06-08-74
US-A- 3537926	03-11-70	None	
FR-A- 2551465	08-03-85	None	
EP-A- 0219945	29-04-87	AU-B- 589208	05-10-89
		AU-A- 6215486	12-03-87
		CA-A- 1250406	28-02-89
		JP-A- 62096303	02-05-87
		US-A- 4770808	13-09-88
US-A- 3756957	04-09-73	None	
US-A- 2086123		None	